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Jui-teng/Lin and Thomas F./George

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Classical Model of Laser-Stimulated Surface
Processes: Energy Absorption Profiles via the
Langevin Equation

Jui-teng Lin and Thomas F. George[†]
Department of Chemistry, University of Rochester
Rochester, New York 14627, USA

A classical model system, consisting of a diatomic molecule chemisorbed on a solid surface and subjected to infrared laser radiation, is presented. A set of coupled equations of motion characterized by the many-body effects of the surface atoms is reduced to the Langevin equations of a two-body problem in transformed coordinates. The surface-induced damping factor and frequency red-shift of the pumped mode are introduced by using a Wigner-Weisskopf-type approximation. The asymmetric forms of the power absorption and the quantized cross section due to the nonlinear effects of the anharmonicity are shown. The energy absorption profiles (energy absorbed vs time), which are universal for any ranges of laser intensity (i.e., as the intensity changes the profile remains the same provided the time scale is changed appropriately) are plotted for different sets of the damping factor and the detuning. It is found that much longer time scales (microsecond) are required for low-power excitations than for the high-power cases. The advantage and difficulties of the normal-mode method and the numerical method are discussed, and a new set of coupled equations in the rotating frame are developed. The energy absorption profiles generated by a numerical method of a CO/Ni system are shown.

I. Introduction

The interaction of infrared radiation with species chemisorbed on a solid surface has been extensively studied recently.¹⁻¹³ In our previous papers, the potential importance of laser-stimulated surface phenomena in heterogeneous systems (migration, recombination, desorption and rate processes) in chemical industry and material science was pointed out.⁹ The possibility of controlling surface phenomena by means of low-power radiation was presented by a simple kinetic model combining the laser rate equation and the Langmuir equation.⁸ Experimental evidence has suggested that laser-stimulated surface processes (LSSP) may be characterized by selective excitations and hence are nonthermal in nature.¹ The nature of LSSP (selective vs nonselective) has been more recently studied by a theoretical model where the level population dynamics of a multilevel system were quantitatively discussed. It was shown, in a quantum mechanical model, that the time scales of LSSP in a heterogeneous system were much longer than those of a gas phase system, due to the fact that the associated laser-power of the former system was much lower than that of the latter system.^{11,12} Furthermore, the selectivity of the pumped mode, essentially characterized by the ratio of the pumping rate and the energy relaxation rate, was analyzed in terms of a competition between multiphoton and multiphonon processes. For high selectivity, a long lifetime (i.e., a weak damping) of the excited pumped mode is required.^{12,13}

Most of our previous models have been cast in a quantum mechanical framework, using a microscopic Hamiltonian which is based on the quantizations of the normal modes.⁶⁻¹³ The associated reduced

masses, the coupling factors and the driving force of the quantum Hamiltonian are transformed quantities defined in the normal coordinates and hence are not explicitly expressed as the functions of the original force and the atomic coordinates before the normal transformation. Hence, some of the features of the original physical system are not clearly displayed in quantum mechanical calculation. We have thus undertaken a study of a model system based on a classical Lagrangian where the masses and the driving forces are defined in terms of the real atomic coordinates. From a classical model we may investigate more details of the physical picture of a real system (e.g., how the active modes and the associated generalized force may be generated and singled out from the bath modes), which may not be readily available in a quantum formulation.

In the present paper, we shall present a classical model described by a Lagrangian of a system consisting of ad molecules chemisorbed on a solid surface. The many-body problem due to the interactions among the ad molecules and the surface atoms will be reduced to a two-body problem, and then the absorption cross section of the system and the stored energies of the pumped modes will be computed analytically. The nature of LSSP and the excitation time scales, essentially characterized by the damping factor of the pumped mode, will be discussed in light of numerical results based on a set of classical equations of motion.

In Section II, a model system described by a classical Lagrangian, including the anharmonicities of the ad molecule and the many-body couplings of both single phonons and multiphonons is presented. A set of transformed equations of motion containing some

important physical features is discussed. In Section III, the Langevin equation of a reduced two-body problem of single-phonon processes is developed, where the many-body effects of the surface atoms are replaced by a damping factor and frequency red-shift of the pumped mode. We then obtain the power absorption and the associated cross section (in a quantization form) of the system by solving the Langevin equation. The steady-state energies stored in the pumped modes are computed.

The universal energy absorption profiles and the time scales of LSSP for arbitrary laser-powers ($10 \text{ W/cm}^2 - 10^{12} \text{ W/cm}^2$) are shown in Section IV. The discussion on the normal-mode method and a set of new coupled equations in the rotating frame, which enables us to overcome some difficulties of the usual numerical methods, are presented in Section V. Finally, we close the paper in Section VI with a summary and conclusion of the main features of LSSP.

II. Transformed Equations of Motion of a Many-Body System

We consider a model system (as shown in Fig. 1) with a diatomic molecule (admolecule) chemisorbed on a solid surface and subject to infrared laser radiation. The Lagrangian may be written as:

$$\mathcal{L} = \mathcal{L}_0 + \sum_i x_i F_i(t), \quad (1)$$

$$\begin{aligned} \mathcal{L}_0 = & \sum_{i=1,2} m_i \left[\frac{1}{2} (\dot{x}_i^2 - \omega_i^2 x_i^2) - \varepsilon_{1i} x_i^3 - \varepsilon_{2i} x_i^4 \right] \\ & + \frac{1}{2} \sum_{j=3} m_j (\dot{x}_j^2 - \omega_j^2 x_j^2) + \frac{1}{2} \sum_{i>j} \lambda_{ij} x_i x_j \\ & + \sum_{p=2} \sum_{i>j} \frac{1}{(p+1)!} \lambda_{ij}^{(p)} x_i x_j^p + \dots, \end{aligned} \quad (2)$$

where m_i , x_i , ω_i ($i=1,2,3,\dots$) are the mass, the displacement and the frequency of the i -th atom, respectively, and the interaction terms with coupling constants λ_{ij} and $\lambda_{ij}^{(p)}$ (between the i -th and j -th atoms) are referred to as the single-phonon (linear) coupling and the p -phonon (nonlinear) coupling, respectively. Here the admolecule is treated as an anharmonic oscillator (up to the quartic terms) while the surface atoms are treated harmonically. The anharmonicities ϵ_{11} , ϵ_{21} and the coupling constant λ_{12} are related to the derivatives of the potential energies and, e.g., for a Morse potential

$$V(x_1, x_2) = D_e \left[1 - e^{-a(x_1 - x_2 - x^0)} \right]^2, \quad (3)$$

we have $\epsilon_{11} = -a^3 D_e$, $\epsilon_{12} = 7a^4 D_e / 12$, and $\lambda_{12} = 2a^2 D_e$. Similarly, the coupling constants λ_{ij} and $\lambda_{ij}^{(p)}$ are related to the pair potential energy between the i -th and j -th atoms by

$$\lambda_{ij} = \left(\frac{\partial^2 V(x_i, x_j)}{\partial x_i \partial x_j} \right)_0, \quad \lambda_{ij}^{(p)} = \left(\frac{\partial^{p+1} V(x_i, x_j)}{\partial x_i \partial x_j^p} \right)_0. \quad (4)$$

The second term in eq.(1) is the interaction energy between the admolecule/surface system and the laser field,

$$F_i(t) = q_i E_i \cos(\omega t) \cos(\theta_i), \quad (5)$$

where q_i is the classical effective charge of the atoms, and θ_i is the angle between the linearly polarized electric field E_i (with circular frequency ω) and the coordinate vector for the optical active mode(s) of the system.

The equations of motion associated with the general form of the Lagrangian given in eq.(1), in principle, may be solved by

the normal mode treatment or directly solved by computational method. However, neither of the above methods is tractable due to the complicated many-body effects of the surface atoms. For the purpose of some analytical results, we shall consider a less general Lagrangian, viz., there are no explicit interactions assumed among the surface atoms and the interaction energy between the adatoms is assumed to be proportional to the product of the displacement from their equilibrium positions.¹⁴ Under these assumptions and the orthogonal transform

$$\chi_1 = \frac{1}{\sqrt{\lambda_{1j}^2 + \lambda_{2j}^2}} (\lambda_{1j} Q_2 + \lambda_{2j} Q_1), \quad (6.a)$$

$$\chi_2 = \frac{1}{\sqrt{\lambda_{1j}^2 + \lambda_{2j}^2}} (\lambda_{2j} Q_2 - \lambda_{1j} Q_1), \quad (6.b)$$

$$\chi_j = Q_j, \quad j \geq 3. \quad (6.c)$$

the Lagrangian of the model system becomes, in the transformed normal mode coordinates Q_i ($i = 1, 2, 3, \dots$),

$$\begin{aligned} \mathcal{L}(Q_1, Q_2, \dots, Q_j, \dots) = & \sum_{i=1,2} M_i \left[\frac{1}{2} \dot{Q}_i^2 - \frac{1}{2} \Omega_i^2 Q_i^2 - \frac{1}{3} K_i Q_i^3 - \frac{1}{4} K'_i Q_i^4 \right] \\ & + \frac{1}{2} M_s \sum_{j=3} (\dot{Q}_j^2 - \Omega_j^2 Q_j^2) + \Lambda Q_1 Q_2 + Q_2 \sum_{j=3} \lambda_j Q_j \\ & + Q_1 \sum_{j=3} \sum_{p=2} \bar{\lambda}_j^{(p)} Q_j^p + Q_2 \sum_{j=3} \sum_{p=2} \lambda_j^{(p)} Q_j^p \\ & + M \dot{Q}_1 \dot{Q}_2 + \sum_i f_i Q_i, \end{aligned} \quad (7)$$

where the transformed frequencies are given by

$$\Omega_{1,2}^2 = \frac{m_1 \lambda_{2j,1j}^2 \omega_1^2 + m_2 \lambda_{1j,2j}^2 \omega_2^2 \pm \lambda_{12} \lambda_{1j} \lambda_{2j}}{M_{1,2} \lambda_j^2}, \quad (8.a)$$

$$\Omega_j \equiv \omega_j, \quad j \geq 3, \quad (8.b)$$

the transformed masses by

$$M_{1,2} = (m_1 \lambda_{j,2j}^2 + m_2 \lambda_{2j,1j}^2) / \lambda_j^2, \quad (8.c)$$

$$M_s = m_j, \quad j \geq 3, \quad (8.d)$$

$$M^- = \lambda_{1j} \lambda_{2j} (m_1 - m_2) / \lambda_j^2, \quad (8.e)$$

the transformed new anharmonicities by

$$K_{1,2} = \frac{3[(\epsilon_{11} \lambda_{2j,1j}^3 + \epsilon_{22} \lambda_{1j,2j}^3) + \lambda_{12}^{(2)} (\lambda_{2j} \lambda_{1j}^2 + \lambda_{1j} \lambda_{2j}^2)]}{\lambda_j^3}, \quad (8.f)$$

$$K'_{1,2} = \frac{\epsilon_{41} \lambda_{2j,1j}^4 + \epsilon_{42} \lambda_{1j,2j}^4}{\lambda_j^4}, \quad (8.g)$$

and the transformed generalized forces by

$$f_{1,2}(t) = (\lambda_{2j,1j} F_1 + \lambda_{1j,2j} F_2) / \lambda_j, \quad (9.a)$$

$$f_j(t) = F_j(t), \quad j \geq 3. \quad (9.b)$$

The new coupling constants (note - these are surface-atom site-dependent) are defined by

$$\Lambda = \frac{\lambda_{12}}{2\lambda_j^2} [(\lambda_{2j}^2 - \lambda_{1j}^2) - \frac{2\lambda_{1j}\lambda_{2j}}{\lambda_{12}} (m_1 \omega_2^2 - m_2 \omega_1^2)], \quad (10.a)$$

$$\lambda_j = (\lambda_{1j}^2 + \lambda_{2j}^2)^{1/2}, \quad (10.b)$$

$$\lambda_j^{(p)} = \frac{\lambda_{1j}^{(p)} \lambda_{1j} + \lambda_{2j}^{(p)} \lambda_{2j}}{(p+1)!}, \quad (10.c)$$

$$\bar{\lambda}_j^{(p)} = \frac{\lambda_{1j}^{(p)} \lambda_{2j} - \lambda_{2j}^{(p)} \lambda_{1j}}{(p+1)!}. \quad (10.d)$$

In deriving eqs. (7)-(10), we have neglected the high-order anharmonic

terms (Q_i^n , $n > 4$) and considered the linear coupling terms between Q_1 and Q_2 while keeping the high-order couplings among the adatoms and the surface atoms. Moreover, the couplings among the surface atoms ($Q_i Q_j$, $i, j > 2$), which give rise to an infinite number of coupled equations of motion, are effectively absorbed into the site-dependent coupling constants (λ_{1j} , λ_{2j}) and the frequency dispersion of the surface-phonon modes (will be characterized by the phonon mode spectrum).

The corresponding equations of motion in the transformed normal coordinates are¹⁵

$$\frac{d}{dt} \left(\frac{\partial \mathcal{L}}{\partial \dot{Q}_i} \right) - \frac{\partial \mathcal{L}}{\partial Q_i} = 0, \quad i = 1, 2, 3, \dots \quad (11)$$

and by substituting from eq. (7),

$$\ddot{Q}_1 + \frac{M}{M_1} \ddot{Q}_2 + \Omega_1^2 Q_1 + K_1 Q_1^2 + K_1' Q_1^3 = \frac{1}{M_1} \left[\Lambda Q_2 + \sum_{j=3} \sum_{p=2} \bar{\lambda}_j^{(p)} Q_j^p + f_1(t) \right] \quad (12.a)$$

$$\ddot{Q}_2 + \frac{M}{M_2} \ddot{Q}_1 + \Omega_2^2 Q_2 + K_2 Q_2^2 + K_2' Q_2^3 = \frac{1}{M_2} \left[\Lambda Q_1 + \sum_{j=3} \lambda_j Q_j + \sum_{j=3} \sum_{p=2} \lambda_j^{(p)} Q_j^p + f_2(t) \right] \quad (12.b)$$

$$\ddot{Q}_j + \Omega_j^2 Q_j = \frac{1}{M_j} \left[\lambda_j Q_2 + \sum_{p=2} p \bar{\lambda}_j^{(p)} Q_j^{p-1} Q_2 + \sum_{p=2} p \lambda_j^{(p)} Q_j^{p-1} Q_1 + f_j(t) \right] \quad (12.c)$$

The above equations of motion describe an ad molecule/surface system with normal frequencies Ω_1 , Ω_2 and Ω_j subject to the generalized forces $f_1(t)$, $f_2(t)$ and $f_j(t)$, respectively. The important features of these transformed equations of motion are (see Fig. 2):

- (1) the transformation [eq. (6)] eliminates linearly coupling between the Ω_1 mode and the surface phonon modes [i.e., no $\lambda_j Q_j$ in eq. (12.a)];
- (2) the Ω_1 mode strongly coupled to the Ω_2 mode (via the ΛQ_2 term), is almost singled out of the low frequencies surface phonon modes, since there is no single-phonon coupling in eq. (12.a) and the p -phonon couplings [via $\bar{\lambda}_j^{(p)} Q_j^p$] are much weaker processes (based on the concept of the energy-gap law);^{13,16}
- (3) from the expressions of

the generalized forces [eq.(9)]. We note that the transformed applied field $f_1 \gg f_2$, for the case of $\lambda_{1j} \approx \lambda_{2j}$ and $q_2 \approx -q_1$, suggests that the Ω_1 mode of the admolecule [corresponding to an asymmetric mode - see eq.(8.a)] may be selectively excited without significantly heating the whole system by means of a radiation field with frequency $\omega \approx \Omega_1$.¹² We also note for the situation of $\lambda_{2j} \gg \lambda_{1j}$ and $q_2 \approx -q_1$ that f_2 may be comparable to f_1 , and hence either Ω_1 or Ω_2 may be optically active depending on the field frequency $\omega \approx \Omega_1$ or $\omega \approx \Omega_2$.

III. Langevin Equation of Reduced Two-Body System

The difficulties of obtaining exact or analytical solutions of the coupled equations [eq.(12)] are twofold: (1) the anharmonic terms of the equations of motion, in general, will lead to time-dependent nonlinear coefficients in the second order differential equations; (2) the many-body effects of the surface phonon modes, characterized by the site-dependent coupling factors, λ_j , $\lambda_j^{(p)}$ etc., will rule out any tractable results when the dimension of j is large. In this section we shall use an iterative scheme to investigate possible solutions of the coupled equations and in turn compute the power absorption and stored energy of the system. We shall first try to linearize the anharmonic terms and then treat the many-body couplings by some physically reasonable approximations. As mentioned in the previous section, the multiphonon couplings (characterized by $\lambda_j^{(p)} Q_j^p$) are in general much weaker than that of the single-phonon (characterized by the linear term $\lambda_j Q_j$). This may be realized by the fact that the p -phonon coupling constant $\lambda_j^{(p)}$ [see eqs.(4) and (10)] is a strongly decreasing function of the multiphonon order p .¹³ We shall now examine the single-phonon processes

and neglect the multiphonon terms for the purpose of a simple treatment of the many-body effects.

By employing the asymptotic (or harmonic balance) method of Bogoluikov,¹⁷ the nonlinear coupled equations of motion [eq. (12) with no multiphonon couplings] may be linearized as follows¹⁸

$$\ddot{Q}_1 + \bar{\Omega}_1^2 Q_1 = [\Lambda Q_2 + f_1(x)]/M_1, \quad (13.a)$$

$$\ddot{Q}_2 + \bar{\Omega}_2^2 Q_2 = [\Lambda Q_1 + \sum_{j=3} \lambda_j Q_j + f_2(x)]/M_2, \quad (13.b)$$

$$\ddot{Q}_j + \Omega_j^2 Q_j = \lambda_j Q_2/M_2, \quad j \geq 3. \quad (13.c)$$

We have introduced the effective frequencies Ω_1 and Ω_2 which are approximately related to the anharmonicities (K_1^* , K_2^*) and the steady-state amplitudes of the modes (A_1 , A_2) by

$$\bar{\Omega}_{1,2} = \Omega_{1,2} - K_{1,2}^* A_{1,2}^2, \quad (14.a)$$

where

$$K_{1,2}^* = \frac{5K_{1,2}}{12\Omega_{1,2}^3} - \frac{3K'_{1,2}}{8\Omega_{1,2}}. \quad (14.b)$$

In eq. (13.c), the field acting on the Q_j -mode has been dropped since the low-frequency surface phonon modes [Ω_j ($j \geq 3$) $\ll \omega$, which are far off-resonant] are not infrared active. In eqs. (13.a) and (13.b), the terms of $(M^-/M_2)\ddot{Q}_2$ and $(M^-/M_1)\ddot{Q}_1$ are also neglected since $M^- \ll M_1, M_2$ for $\lambda_{1j} < \lambda_{2j}$ and $m_1 \approx m_2$ [referred to eq. (8)].

We shall next use a technique, which enabled us to reduce a multi-level system to a few-level system in our previous quantum mechanical models,^{11,12} to reduce the many-body classical problem to a few-body problem. To establish the iterative scheme, let us represent the zeroth-order, first-order homogeneous solutions of the

coupled equations by $Q^{(0)}$ and $Q^{(1)}$, respectively, and choose the initial conditions to be: $Q_1(0) = A_0$, $Q_2(0) = B_0$, $Q_j(0) = A_j$ ($j \geq 3$), $\dot{Q}_i(0) = 0$ (for all i). By eq. (13.b) we get

$$Q_2^{(0)}(t) = B_0 \cos(\bar{\Omega}_2 t), \quad (15)$$

and using eq. (15) we find the homogeneous solution of eq. (13.c) as

$$Q_j^{(1)}(t) = A_j \cos(\Omega_j t) + \frac{\lambda_j}{M_s \Omega_j} \int_0^t dt' \sin(\Omega_j t') Q_2^{(0)}(t-t'). \quad (16)$$

Decomposing $Q_2^{(0)}(t-t')$ by eq. (15) and its derivative, we have

$$Q_2^{(0)}(t-t') = Q_2^{(0)}(t) \cos(\bar{\Omega}_2 t') - \frac{1}{\bar{\Omega}_2} \dot{Q}_2^{(0)}(t) \sin(\bar{\Omega}_2 t'). \quad (17)$$

Substituting eq. (17) into eq. (16) and working out the integrals by approximating the upper limit from t to infinity, we obtain

$$Q_j^{(1)}(t) = A_j \cos \Omega_j t + \frac{\lambda_j}{2M_s} P\left(\frac{1}{\Omega_j^2 - \bar{\Omega}_2^2}\right) Q_2^{(0)}(t) - \frac{\pi \lambda_j}{2M_s \Omega_j \bar{\Omega}_2} [\delta(\Delta_j) - \delta(\Delta_j^+)] \dot{Q}_2^{(0)}(t), \quad (18)$$

where $\Delta_j = \bar{\Omega}_2 - \Omega_j$, $\Delta_j^+ = \Omega_2 + \Omega_j$, and P denotes the principal part. In arriving at eq. (18), we have used the relation¹⁹

$$\lim_{t \rightarrow \infty} \int_0^t e^{\pm i \Delta t'} dt' = \pi \delta(\Delta) \pm i P\left(\frac{1}{\Delta}\right). \quad (19)$$

Substituting eq. (18) into eq. (13.b) and using the Wigner-Weisskopf-type approximation,¹⁹ i.e., replacing the sum over the phonon modes by the integral over the associated phonon mode density of states $\rho(\Omega_j)$, we find the first-order solution of eq. (13.b) to be embodied by the Langevin equation:

$$\langle \ddot{Q}_2 \rangle + \gamma \langle \dot{Q}_2 \rangle + (\bar{\Omega}_2^2 - \delta\omega) \langle Q_2 \rangle = [\Lambda \langle Q_1 \rangle + f_1(t) + \langle f_s(t) \rangle] / M_2 \quad (20)$$

where $\langle \dots \rangle$ denotes the ensemble average over the surface temperature,

and $\langle f_s \rangle$ is the surface fluctuation force given by

$$\langle f_s(t) \rangle = \left\langle \sum_{j=3} \lambda_j A_j \cos(\Omega_j t) \right\rangle. \quad (21)$$

γ and $\delta\omega$, the damping factor and frequency shift, respectively, are related to the coupling constant λ_j and the phonon density of states ρ by

$$\gamma = \frac{\pi}{2} \frac{\lambda_j^2(\bar{\Omega}_2)}{M_2 M_s \bar{\Omega}_2^2} \rho(\bar{\Omega}_2), \quad (22.a)$$

$$\delta\omega = \frac{1}{M_s} \int_0^\infty d\Omega_j \frac{\lambda_j^2(\Omega_j)}{M_2} \frac{\rho(\Omega_j)}{\Omega_j^2 - \bar{\Omega}_2^2}. \quad (22.b)$$

The above classical results [eq.(22)] are in exact agreement with our previous quantum mechanical results where the level broadening and the level shift correspond to the damping factor and the frequency shift, respectively.^{9,12} It is important to note that, in eq.(22.a), both the coupling constant $\lambda_j(\bar{\Omega}_2)$ and the phonon mode density $\rho(\bar{\Omega}_2)$ are evaluated at the frequency of the Ω_2 -mode which is coupled to the surface phonon modes. For a Debye model spectrum $\rho(\Omega_j) = 3\Omega_j^2/\Omega_D$ with the cutoff frequency Ω_D , we obtain

$$\gamma = 3\pi \lambda_j^2(\bar{\Omega}_2) / (2M_2 M_s \Omega_D^3), \quad (23.a)$$

$$\delta\omega = \frac{3\lambda_j^2(\bar{\Omega}_2)}{M_2 M_s \Omega_D^2} \left[1 - \frac{\bar{\Omega}_2}{2\Omega_D} \ln \left| \frac{\Omega_D + \bar{\Omega}_2}{\Omega_D - \bar{\Omega}_2} \right| \right]. \quad (23.b)$$

We also note that in eq.(20) the new frequency is red-shifted to the lower frequency $(\bar{\Omega}_2^2 - \delta\omega)^{1/2}$ since $\delta\omega$ is a positive quantity for $\bar{\Omega}_2 < \Omega_D$ [see eq.(23.b)]. For instance, the frequency of isolated CO, $\Omega_2 = 2145 \text{ cm}^{-1}$, may be red-shifted to 1932 cm^{-1} and 2069 cm^{-1} when it

is chemisorbed on a nickel surface with on-top site and bridge site, respectively.²¹

So far, we have reduced the many-body problem to a two-body problem described by the equations of motion (13.a) and (20), where the surface-induced damping factor and frequency shift of the Ω_2 -mode are introduced through the Langevin equation. We shall now solve the equations and compute the power absorption and the stored energy of the pumped mode(s). For the case of low surface temperature (i.e., $\langle f_s \rangle \approx 0$), the general solutions of the coupled equations (13.a) and (20) are found to be in the form

$$\begin{pmatrix} \langle Q_1(t) \rangle \\ \langle Q_2(t) \rangle \end{pmatrix} = \sum_{i=1}^4 \begin{pmatrix} A_i & A_{11} & A_{12} \\ B_i & A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} e^{R_i t} \\ \sin(\omega t) \\ \cos(\omega t) \end{pmatrix}, \quad (24)$$

where R_i are the roots of the equation

$$X^4 + rX^3 + (\bar{\Omega}_1^2 + \bar{\Omega}_2^2)X^2 + r\bar{\Omega}_1^2 X + (\bar{\Omega}_1 \bar{\Omega}_2)^2 - \Lambda/(M_1 M_2) = 0. \quad (25)$$

The general solutions are complicated due to their transient parts. However, for a sufficient time, the transient solutions vanish, and the motion of the modes follows the frequency of the field with the steady-state solutions given by

$$\begin{pmatrix} \langle Q_1^{ss}(t) \rangle \\ \langle Q_2^{ss}(t) \rangle \end{pmatrix} = \begin{pmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{pmatrix} \begin{pmatrix} \sin(\omega t) \\ \cos(\omega t) \end{pmatrix}, \quad (26)$$

where

$$A_{ij} = D_{ij}/D, \quad i, j = 1, 2, \quad (27)$$

$$D_{11} = r\omega\Lambda(M_2 C_1 V_2 + \Lambda V_1)/(M_1 M_2), \quad (28.a)$$

$$D_{21} = r\omega C_1 (M_2 C_1 V_2 + \Lambda V_1)/M_2, \quad (28.b)$$

$$D_{12} = \frac{\Lambda V_2}{M_1^2 M_2} (C_1 C_2 M_1 - \Lambda^2) + C_1 V_1 \left(C_2^2 + r^2 \omega^2 - \frac{\Lambda^2 C_2}{C_1 M_1 M_2} \right), \quad (28.c)$$

$$D_{22} = \left(C_1 V_2 + \frac{\Lambda V_1}{M_2} \right) \left(C_1 C_2 - \frac{\Lambda^2}{M_1 M_2} \right), \quad (28.d)$$

$$D = (r \omega C_1)^2 + \left[\left(\frac{\Lambda}{M_1 M_2} \right)^2 - C_1 C_2 \right]^2, \quad (29.a)$$

$$C_1 = \bar{\Omega}_1^2 - \omega^2, \quad (29.b)$$

$$C_2 = \bar{\Omega}_2^2 - \omega^2, \quad (29.c)$$

$$\bar{\Omega}_2 = (\bar{\Omega}_2^2 - \delta \omega)^{1/2}. \quad (29.d)$$

and the applied field coupling terms are [see eqs.(5) and (9)]

$$V_1 = [\lambda_{ij} g_{i1} E_1 \cos(\theta_1) - \lambda_{ij} g_{i2} E_2 \cos(\theta_2)] / (\lambda_{ij} M_1), \quad (30.a)$$

$$V_2 = [\lambda_{ij} g_{i1} E_1 \cos(\theta_1) + \lambda_{ij} g_{i2} E_2 \cos(\theta_2)] / (\lambda_{ij} M_2). \quad (30.b)$$

Combining eqs.(9) and (30) and the derivative of eq.(27), we obtain the steady-state instantaneous power absorption (force times velocity) of the total system (admolecule/surface) via the optically active modes - A mode (with frequency $\bar{\Omega}_1$) and B mode (with frequency $\bar{\Omega}_2$) as follows:

$$\langle P_T(t) \rangle = \sum_{i=1}^2 f_i(t) \langle \dot{Q}_i^{s.s.}(t) \rangle \equiv \langle P_A(t) \rangle + \langle P_B(t) \rangle, \quad (31.a)$$

where

$$\begin{pmatrix} \langle P_A(t) \rangle \\ \langle P_B(t) \rangle \end{pmatrix} = \omega \begin{pmatrix} V_1 A_{11} - \frac{V_1 A_{12}}{2} \\ V_2 A_{21} - \frac{V_2 A_{22}}{2} \end{pmatrix} \begin{pmatrix} M_1 \cos^2(\omega t) \\ M_2 \sin(2\omega t) \end{pmatrix}. \quad (31.b)$$

Since the $\sin(2\omega t)$ term vanishes as a result of time averaging over the period of the field, we immediately obtain the steady-state average power absorption

$$\overline{\langle P_A(t) \rangle} = M_1 \omega V_1 A_{11} / 2, \quad (32.a)$$

$$\overline{\langle P_B(t) \rangle} = M_2 \omega V_2 A_{21} / 2. \quad (32.b)$$

The corresponding classical absorption cross section, defined by [power absorption]/[laser intensity], is given by (in cgs units)

$$\sigma^{class} = \frac{8\pi}{cE^2} (\langle \overline{P_A(t)} \rangle + \langle \overline{P_B(t)} \rangle) \quad (33.a)$$

Upon quantization this yields the quantum absorption cross section for a transition between levels n and $(n+1)$ of a quantum system^{10,18}

$$\sigma^{quan} \propto \sum_{n=1}^2 \frac{(n+1) \overline{\Gamma}_n}{[\Delta_i - 2\epsilon_i^*(n+1/2)]^2 + \overline{\Gamma}_n^2} \quad (33.b)$$

where Δ_i is the detuning $\Delta_i = \overline{\Omega}_i - \omega$ and ϵ_i^* is the anharmonicity.

Note that the absorption cross section is not a symmetric Lorentzian due to the nonlinear effect, $2\epsilon^*(n+1/2)$, and the optimum detuning for maximum absorption cross section is laser intensity dependent (see Ref. 10 for more rigorous discussions).

Using the steady-state solutions [eq.(27)], we may easily obtain the average stored energies (for steady-state) in the pumped A and B modes, given by \overline{E}_A and \overline{E}_B , respectively, as follows:

$$\overline{E}_{A,B} = \frac{M_1}{2} \langle \overline{\dot{Q}_{1,2}^{ss}(t)} \rangle^2 + \frac{M_2}{2} \overline{\Omega_{1,2}^2} \langle \overline{Q_{1,2}^{ss}(t)} \rangle^2, \quad (34.a)$$

$$\overline{E}_A = \frac{M_1}{4} (\overline{\Omega}_1^2 + \omega^2) (A_{11}^2 + A_n^2), \quad (34.b)$$

$$\overline{E}_B = \frac{M_2}{4} (\overline{\Omega}_2^2 + \omega^2) (A_{21}^2 + A_n^2). \quad (34.c)$$

For the case of $\Lambda \approx 0$ and $\omega \approx \Omega_2$, the stored energies reduce to the simple forms

$$\overline{E}_A = M_1 (\overline{\Omega}_1^2 + \omega^2) \left[\frac{V_1}{2(\overline{\Omega}_1^2 - \omega^2)} \right]^2, \quad (34.d)$$

$$\overline{E}_B = \frac{M_2 V_2^2}{8} \left[\frac{r}{(\overline{\Omega}_2 - \omega)^2 + (r/2)^2} \right]^2. \quad (34.e)$$

This is the situation of very weak coupling between the A and B modes where the B mode is almost isolated from the A mode but coupled to

the bath (surface phonon) modes via the damping factor γ . We note that for the weak damping case (i.e., the pumped B mode has a very long lifetime), one may selectively excite the B mode without significantly "heating" the other modes. A more quantitative description of the dynamical nature of the selective and nonselective excitations has been recently presented for a quantum mechanical system.^{11,12}

IV. Universal Energy Absorption Profiles

In the previous section, we have reduced the many-body problem to a two-body problem where the many-body effects are replaced by including a damping factor and a frequency shift in the Langevin equations. In the two-body problem, the general solutions of the coupled equations of motion are still intractable due to the non-explicit forms of the transient solutions [eq.(24)]. Instead of evaluating the steady-state stored energies [eq.(34)], we shall now investigate the time evolution of the energy absorption of the pumped mode by further reducing the two-body problem to a single-body problem. For this purpose, we consider the situation where only the B mode is resonantly pumped ($\omega \approx \bar{\Omega}_2$) being weakly coupled to the A mode ($\Lambda \ll f_2$) but strongly coupled to the surface phonon modes (via the damping factor γ). The Langevin equation [eq.(20)], neglecting the surface fluctuating force $\langle f_s \rangle$, becomes the equation of motion of a damped anharmonic oscillator subject to a generalized force $f_2(t) = M_2 V_2 \cos(\omega t)$,

$$\langle \ddot{Q}_2(t) \rangle + \gamma \langle \dot{Q}_2(t) \rangle + \bar{\Omega}_2^2 \langle Q_2(t) \rangle = V_2 \cos(\omega t). \quad (35)$$

The complete solution of eq.(35) is found to be

$$\begin{aligned} \langle Q_2(t) \rangle = & A_{ss} \sin(\omega t) + A_{ss} \cos(\omega t) \\ & + e^{-\frac{\gamma t}{2}} [A_0 \cos(\omega_1' t) + B_0 \sin(\omega_1' t)], \end{aligned} \quad (36)$$

with the initial values $A_0 = \langle Q_2(0) \rangle$, $B_0 = [\langle \dot{Q}_2(0) \rangle + r \langle Q_2(0) \rangle / 2] / \omega'_2$, where

$$\omega'_2 = [\bar{\Omega}_2^2 - (r/2)^2]^{1/2}, \quad (37.a)$$

$$A_{ad} = r \bar{\Omega}_2 V_2 / \bar{Z}, \quad (37.b)$$

$$A_{el} = (\bar{\Omega}_2^2 - \omega^2) V_2 / \bar{Z}, \quad (37.c)$$

$$\bar{Z} = (\bar{\Omega}_2^2 - \omega^2)^2 + (r\omega)^2, \quad (37.d)$$

$$\bar{\Omega}_2^2 = \bar{\Omega}_2^2 - \delta\omega. \quad (37.e)$$

The constants A_{ab} and A_{el} are referred to as the absorptive and the elastic amplitudes because the time-averaged power absorption is entirely due to the out-of-phase displacement $A_{ab} \sin(\omega t)$ [which leads to an in-phase velocity with respect to the driving field $V_2 \cos(\omega t)$]. The corresponding stored energy in the pumped B mode is

$$E_B(t) = E_0 \left\{ 1 + e^{-rt} - 2e^{-\frac{rt}{2}} \cos[(\omega'_2 - \omega)t] \right\}, \quad (38.a)$$

where E_0 is the steady-state energy given by

$$E_0 = \frac{e^2}{32M_2} E_{eff}^2 \left[\frac{r}{\Delta_{opt}^2 + (r/2)^2} \right]^2. \quad (38.b)$$

Here we have introduced an effective electric field acting on the B mode [see eq. (9)], for the classical effective charge $e = q_1 = -q_2$,

$$E_{eff} = \frac{\lambda_{ij} E_2 \cos(\theta_2) - \lambda_{ij} E_1 \cos(\theta_1)}{(\lambda_{ij}^2 + \lambda_{ij}^2)^{1/2}}, \quad (39)$$

and the optimum detuning $\Delta_{opt} = \Delta - K_2^* (A_{ab}^2 + A_{el}^2)$ which is laser intensity dependent [see eq. (14)].¹⁰ By using $I(\text{laser intensity}) = E_{eff}^2 / (8\pi/C)$, the steady-state energy may be expressed in a conventional form

$$E_0 = 2.5 \times 10^{-7} \left(\frac{e^2 I}{M_2} \right) \left(\frac{r}{\Delta_{opt}^2 + (r/2)^2} \right)^2. \quad (40)$$

where the units used are: E_0 (eV), I (W/cm²), M_2 (amu), e (4.8×10^{-10} esu), and both the detuning and damping factor are in the units of cm⁻¹.

For the case of $\gamma=0$, we note that the solution of eq.(35) is

$$\langle Q_2(t) \rangle = \frac{2e}{M_2 \Delta_{\text{opt}}} E_{\text{eff}} \sin\left(\frac{\Delta_{\text{opt}} t}{2}\right) \cos\left[\frac{(\omega'_2 + \omega)}{2} t\right], \quad (41)$$

and the corresponding energy absorption of the pumped mode is

$$E_B(t) = \left(\frac{2\pi e^2}{c M_2}\right) E_{\text{eff}}^2 \left(\frac{1 - \cos(\Delta_{\text{opt}} t)}{\Delta_{\text{opt}}^2}\right), \quad (42)$$

which is an oscillatory function since the available energy, for the isolated B mode, will be necessarily transferred back and forth between the pumped mode and the laser field (via absorption and stimulated emission, in "quantum mechanical" language).²² Note that eq.(42) reduces to $E_A(t) = (\pi e^2 / c M_2) I t^2$ which is proportional to t^2 for the exact resonance case.

The energy absorption given by eq.(38) is shown in Fig. 3 for different sets of the optimum detuning Δ_{opt} and the damping factor γ . It is important to note that these energy absorption profiles are universal for all ranges of the laser intensity ($I=10$ W/cm² - 10^{12} W/cm²) when the associated time scales in units of γ^{-1} are chosen. From eqs.(38) and (40), we may define the time scales (in units of γ^{-1}) by relating the laser intensities (I_1 and I_2) and the damping factors (γ_1 and γ_2) by

$$(\gamma_2^{-1} / \gamma_1^{-1}) = (I_2 / I_1)^{1/2} \quad (43)$$

For instance, curve(D) in Fig. 3 describes the time dependence of the

energy absorption of the pumped mode for the low power case $I_1 = 10^2 \text{ W/cm}^2$ with the time scale $\gamma_1^{-1} = 1.3 \times 10^{-7}$, as well as for the high power case $I_2 = 10^8 \text{ W/cm}^2$, but the time scale is reduced to [by eq.(43)] $\gamma_2^{-1} = \gamma_1 \times 10^{-3}$. It is seen from these universal energy absorption profiles that the energies reach the steady-state values in the micro-second time scale for the low power case ($I \sim 10^2 \text{ W/cm}^2$) while being in the nanosecond region for the high power case ($I \sim 10^8 \text{ W/cm}^2$) and picosecond for $I \sim 10^{12} \text{ W/cm}^2$. This is one of the important features of laser-stimulated surface processes, where low-power radiation ($I = 10\text{-}100 \text{ W/cm}^2$) may be used to study the adspecies/surface system in a much longer time scale compared to that of a gas-phase system (e.g., multiphoton dissociation of polyatomic molecules like SF_6).^{11,12} It should also be noted that for selective excitations by means of low-power radiation to be possible, one requires not only a long lifetime of the pumped mode (i.e., small damping factor) but also a well-defined laser frequency such that the optimum detuning Δ_{opt} and the damping factor γ both have the small values like $10^{-3} - 10^{-4} \text{ cm}^{-1}$ [see eq.(40)].

For a comparison of the energy absorption profiles given by the reduced single-body Langevin equation [eq.(35)] and those of a set of coupled equations, we show in Fig. 4 the numerical results obtained by solving the classical equations of motion are for a model system of CO/Ni .²³ We see that the energy absorption curve shown in Fig. 4 is different from curve (D) in Fig. 3 by the fluctuation (broadening) feature of the energy absorption. In the single-body problem, we obtain only the average value of the fluctuating energy, whereas by directly solving a many-body problem we may investigate

in detail fast oscillations of the energy absorption profile caused by the energy relaxation of the pumped mode and the feedback from the surface. We also show the energy absorption profile for the CO/Ni system with $\Delta_{\text{opt}} = \gamma = 0$ in Fig. 5. We see, except for the fluctuating behavior, the resonance excitation curve of eq.(42) $E_A(t) \propto It^2$, as expected in the single-body problem.

V. Discussion

In this section we shall discuss some advantages and difficulties of the normal-mode method and present a set of transformed equations of motion (in the rotating-wave approach), which are more practical in the classical trajectory calculations for the case of low-power excitation processes where a very long time scales are involved.

A. Normal-Mode Method

Consider a Lagrangian in the general form

$$\mathcal{L} = \sum_{i,j} (T_{ij} - V_{ij} + F_{ij}) + \sum_i \gamma_i F_i(t), \quad (44)$$

where T_{ij} , F_{ij} and V_{ij} are the kinetic energy, the dissipation function and the potential energy, respectively:

$$T_{ij} = \frac{1}{2} m_{ij} \dot{x}_i \dot{x}_j, \quad (45.a)$$

$$F_{ij} = \frac{1}{2} \gamma_{ij} \dot{x}_i \dot{x}_j, \quad (45.b)$$

$$V_{ij} = \frac{1}{2} \lambda_{ij} x_i x_j + \sum_{p=2} \frac{1}{(p+1)!} \lambda_{ij}^{(p)} x_i x_j^p + \dots \quad (45.c)$$

The corresponding equations of motion of this dissipative system are given by²⁴

$$\frac{d}{dt} \frac{\partial \mathcal{L}}{\partial \dot{x}_i} = \frac{\partial \mathcal{L}}{\partial x_i} - \frac{\partial F_{ij}}{\partial \dot{x}_i} \quad (46)$$

The normal-mode method capitalizes on the fact that each equation of motion in eq.(46) in the normal coordinates involves only a single coordinate and all the variables are completely separated. However, the mass coefficient m_{ij} and the dissipation factor γ_{ij} are in general functions of the coordinate x_i , and hence a set of normal transforms which simultaneously diagonalizes T_{ij} , F_{ij} and V_{ij} is not in general available.¹⁵ For a physical system consisting of N adatoms chemisorbed on a solid surface, there are $3N$ "frustrated" surface normal modes so that the normal-mode method essentially involves the diagonalization of a $3N \times 3N$ matrix, which is in general not available particularly for the case where the mass coefficient m_{ij} is coordinate-dependent and when N is a big number. For a tractable model, we shall seek a method in which the dimension of a related matrix may be significantly reduced. Consider the case where the total system (subject to a laser field) may be decomposed into two (or more) almost isolated subsystems, then each subsystem involves the diagonalization of a small matrix which is possible by a set of normal transform. Such subsystems may be, in principle, physically possible when there is a big energy gap between them.^{13,16} This decomposition may also be mathematically possible by a set of partially orthogonal transforms, e.g., in Section I where we used the transformed coordinates in eq.(6) to decompose the total system into the Ω_1 mode and a subsystem (Ω_2 mode plus bath modes) with the Ω_1 mode (or/and the Ω_2 mode) able to be selectively excited.

For a simple example, let us consider a system which is decomposed into two subsystems, where subsystem-2 (with l normal modes referred to as the inactive bath modes) is weakly coupled to the

subsystem-1 (with $3N-2$ normal modes referred to as the pumped mode(s)), then the average power absorption of the system is given by

$$\overline{P(t)} = \sum_{i=1}^{3N-2} \frac{\gamma_i f_i \omega^2}{(\omega_i^2 - \omega^2)^2 + (\gamma_i \omega)^2}, \quad (47)$$

where ω_i is a normal frequency of the pumped subsystem with the associated damping factor γ_i and f_i is a transformed generalized forces related to the generalized force in the original coordinates V_j (for driving forces given by $F_j(t) = V_j \cos \omega t$) by

$$f_i = \sum_j C_{ij} V_j \quad (48)$$

where C_{ij} are the elements of the transformation matrix which simultaneously diagonalizes the kinetic energy, dissipation function and potential energy of subsystem-1, but does not necessarily diagonalize those of the subsystem-2.

B. Numerical Method in the Rotating Frame

Consider a model system consisting of adspecies (adatoms-1 and 2) chemisorbed on a solid surface and subject to an external field $[V_1 \sin(\omega t)]$, described by a set of coupled equations (for only the nearest interactions are considered) as

$$m_1 \ddot{x}_1 = - \frac{\partial V_2(x_1, x_2)}{\partial x_1} - m_1 \gamma_1 \dot{x}_1 + V_1 \sin(\omega t) \quad (49)$$

$$m_2 \ddot{x}_2 = - \frac{\partial V_2(x_1, x_2)}{\partial x_2} - \frac{\partial V_3(x_2, x_3)}{\partial x_2} - m_2 \gamma_2 \dot{x}_2 + V_2 \sin(\omega t) \quad (50)$$

$$m_s \ddot{x}_j = - \frac{\partial V_{j-1,j}(x_{j-1}, x_j)}{\partial x_j} - \frac{\partial V_{j,j+1}(x_j, x_{j+1})}{\partial x_j} - m_s \gamma_j \dot{x}_j + V_j \sin(\omega t), \quad j \geq 3, \quad (51)$$

where x_i ($i=1, 2, 3, \dots$) is the coordinate of the i -th atom for the longitudinal motion, and the damping terms $m_i \gamma_i \dot{x}_i$ are included to take into account the lateral interactions between the atoms of one

row with those of another. The damping factors γ_i ($i=1,2$) of the adatoms [which may be expressed in the form of eq.(22.a)] simulate the surface effects of the solid crystal, and the damping factors γ_j ($j \geq 3$) of the solid atoms simulate the effect of the bulk of the lattice in presenting the free translational motion of the one-dimensional linear chain. This is the significant difference of eqs.(49)-(51) from that of the usual one-dimensional chain model, where the latter loses all the many-body surface effects of the adatoms and the many-body bulk effects of the solid atoms.

As discussed in Section IV, the time scales of the energy absorption profiles (in units of γ^{-1}) for the low-power excitations ($I \sim 10^2 \text{ W/cm}^2$) are in the ranges of microseconds, which are much longer than the oscillation cycle of the field ($\omega \sim 10^{14}$ second). This causes the difficulty in obtaining the absorption profiles by a computational method which solves the above coupled equations directly. Furthermore, the energy absorption of the pumped mode is very sensitive to the amount of detuning ($\Delta \equiv \omega_0 - \omega$). For $I \sim 10^2 \text{ W/cm}^2$, we require that $\Delta_{\text{opt}}, \gamma \approx 10^{-3} - 10^{-4} \text{ cm}^{-1}$ which also causes difficulty in tuning the field frequency to obtain optimum excitations. Note that for the cases of high-power excitations ($I > 10^8 \text{ W/cm}^2$), these difficulties would not be encountered and hence we may obtain the absorption profiles numerically from eqs.(49)-(51) [Figs. 4 and 52].

In order to overcome the difficulties described above and obtain the energy absorption profiles by a numerical method, particularly for the low-power excitation processes, we now present a method which relies on the rotating wave approximation (RWA),

a well-known technique for quantum mechanical systems.^{19,22} By using the rotating frame

$$y_i(t) = \chi_i(t) \exp(i\omega_0 t), \quad (52)$$

where ω_0 is the frequency of the optically active mode of the ad-species/surface system, we shall consider the near-resonant excitation with the detuning $\Delta = \omega_0 - \omega \approx 0$ (for the harmonic model) or $\Delta = \omega_0 - K^* A^2 - \omega \approx 0$ [for the anharmonic model - see eq. (14)].

The coupled equations of motion (49)-(51) become

$$m_1 \ddot{y}_1 = -\frac{\partial V_{12}}{\partial y_1} + m_1 \omega_0^2 y_1 - m_1 \gamma_1 (\dot{y}_1 + i\omega_0 y_1) + \frac{V_1}{2} e^{-i\Delta t} \quad (53)$$

$$m_2 \ddot{y}_2 = -\frac{\partial V_{12}}{\partial y_2} - \frac{\partial V_{23}}{\partial y_2} + m_2 \omega_0^2 y_2 - m_2 \gamma_2 (\dot{y}_2 + i\omega_0 y_2) + \frac{V_2}{2} e^{-i\Delta t} \quad (54)$$

$$m_s \ddot{y}_j = -\frac{\partial V_{j-1,j}}{\partial y_j} - \frac{\partial V_{j,j+1}}{\partial y_j} + m_s \omega_0^2 y_j - m_s \gamma_j (\dot{y}_j + i\omega_0 y_j) + \frac{V_j}{2} e^{-i\Delta t}, \quad j \geq 3, \quad (55)$$

where $\Delta \equiv \omega_0 - \omega$ is the detuning. In obtaining eqs. (53)-(55) we have used the RWA, that is, we have neglected the fast oscillating terms $\exp[\pm(\omega_0 + \omega)t]$. The important features of the new equations of motion are: (1) due to the complex coefficients, the j coupled equations are in fact $2j$ real equations (equivalent to $4j$ first-order differential equations which must be numerically solved); (2) the time-dependent field with the very fast sinusoidal function $\sin(\omega t)$ is eliminated in the rotating frame in the RWA and the coupled equations are characterized by the detuning Δ which leads to a much slower oscillating function $\exp(-i\Delta t)$ for near resonance.

Therefore, by using the new set of equations of motion, we are able to compute the energy absorption by solving the coupled equations numerically. It is important to note that the new coupled

equations (53)-(55) may be solved by using, for example, the Runge-Kutta method with a much longer time step ($\approx 10^{-8}$ sec) than for the original coupled equations (49)-(51) ($\approx 10^{-16}$ sec). The applications of the new coupled equations on some real adspecies/surface system, e.g., CO/Ni and H/Pt, are in progress.

VI. Summary of the Main Features of LSSP

We conclude the main feature of LSSP and summarize the specific results obtained in this classical model as follows:

(a) By a set of orthogonal transforms, we are able to generate two normal modes where the high frequency asymmetric (Ω_1) mode is uncoupled to the bath mode while being coupled to the low frequency symmetric (Ω_2) mode. From the transformed frequencies [eq.(8.a)] and the generalized forces [eq.(9.a)], we are able to see some selective nature of the system.

(b) The nonlinear coupled equation due to the anharmonicities of the potential energies may be linearized by the asymptotic (or harmonic balance) method where the amplitude-dependent frequencies are presented in eq.(14).

(c) By the iterative procedure, the many-body effects of the surface atoms are absorbed into the Langevin equation, where a damping factor and frequency red-shift are introduced [eq.(22)]. These classical results are in agreement with those of the quantum mechanical calculation presented in our earlier work, where the Markovian statistics and Wigner-Weisskopf theory were used.⁹⁻¹²

(d) The power absorption and the quantized cross section are obtained by solving the coupled Langevin equations and the asymmetric behavior is shown by the nonlinear effects of the anharmonicities

[eqs.(32) and (33)].

(e) The energy absorption profiles of the pumped mode, which are universal for any laser-power (ranging from 10 W/cm^2 to 10^{12} W/cm^2), are shown for different sets of the damping factor and the detuning [Fig. 3]. The long time scales of LSSP (in the range of microseconds) are discussed for the case of low-power excitations [eq.(43)].

(f) The average power absorption of a system, which may be decomposed into almost isolated subsystems, is computed by the normal-mode method [eq.(47)].

(g) Finally, the difficulties in numerical methods of solving a set of coupled equations are pointed out, and a set of new coupled equations, which enable one to numerically generate the energy absorption curves of low-power LSSP, are presented in the rotating frame [eqs.(53)-(55)].

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Figure Captions

- Fig.1. Diatomic molecule chemisorbed on a solid surface. The coupling constants between the adatom-1 and -2 and among the adatoms and the surface atoms are given by λ_{12} , λ_{1j} and λ_{2j} , respectively.
- Fig.2. Schematic diagram of the density of states for the transformed normal frequencies Ω_1 , Ω_2 and Ω_j given by eq.(8). The coupling factors among different modes are denoted by Λ and λ_j [given by eq.(10)]. Note that the Ω_1 mode is uncoupled to Ω_j modes for the single-phonon processes.
- Fig.3. The universal energy absorption profiles of the pumped mode for different sets of the optimum detuning Δ_{opt} and the damping factor γ (in units of cm^{-1}): curve A - $\Delta_{\text{opt}}=0$, $\gamma=2 \times 10^{-3}$; curve B - $\Delta_{\text{opt}}=0.5\gamma = 5 \times 10^{-4}$; curve C - $\Delta_{\text{opt}}=\gamma=10^{-3}$; curve D - $\Delta_{\text{opt}}=2.5\gamma=2.5 \times 10^{-4}$; curve E - $\Delta_{\text{opt}}=5\gamma=2 \times 10^{-5}$; curve F - $\Delta_{\text{opt}}=8\gamma=10^{-5}$; curve G - $\Delta_{\text{opt}}=10\gamma=10^{-4}$; for low-power laser $I=100\text{W}/\text{cm}^2$. Note that the time scales are shown in units of γ^{-1} .
- Fig.4. Energy absorption of the pumped CO mode in the CO/Ni system for laser-power $I=10^{12}\text{W}/\text{cm}^2$ with $\Delta_{\text{opt}}=0.2\gamma=20\text{cm}^{-1}$.
- Fig.5. Energy absorption of the same system as in Fig.4, but with $\Delta_{\text{opt}}=\gamma=0$.

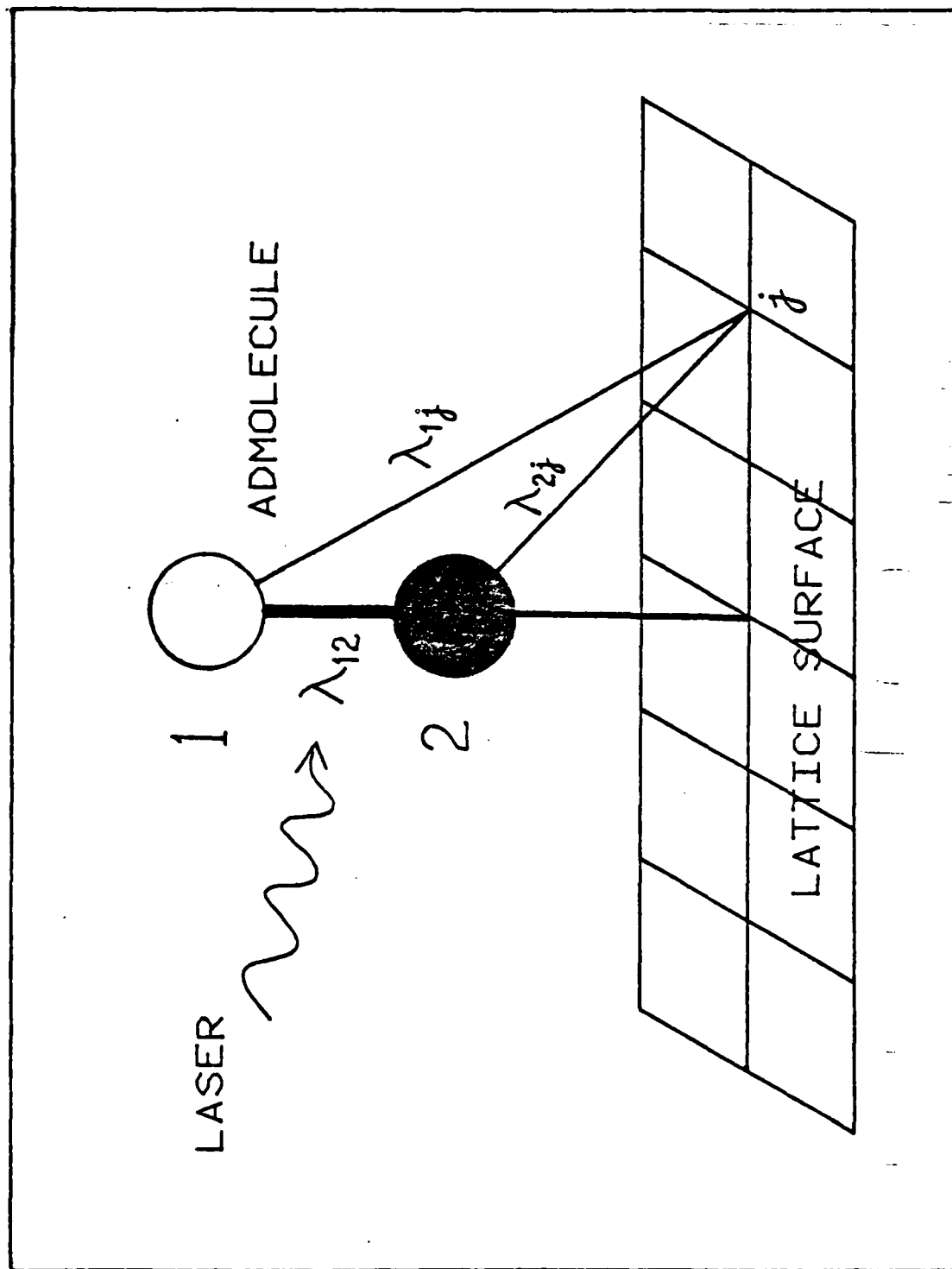


Fig 1.

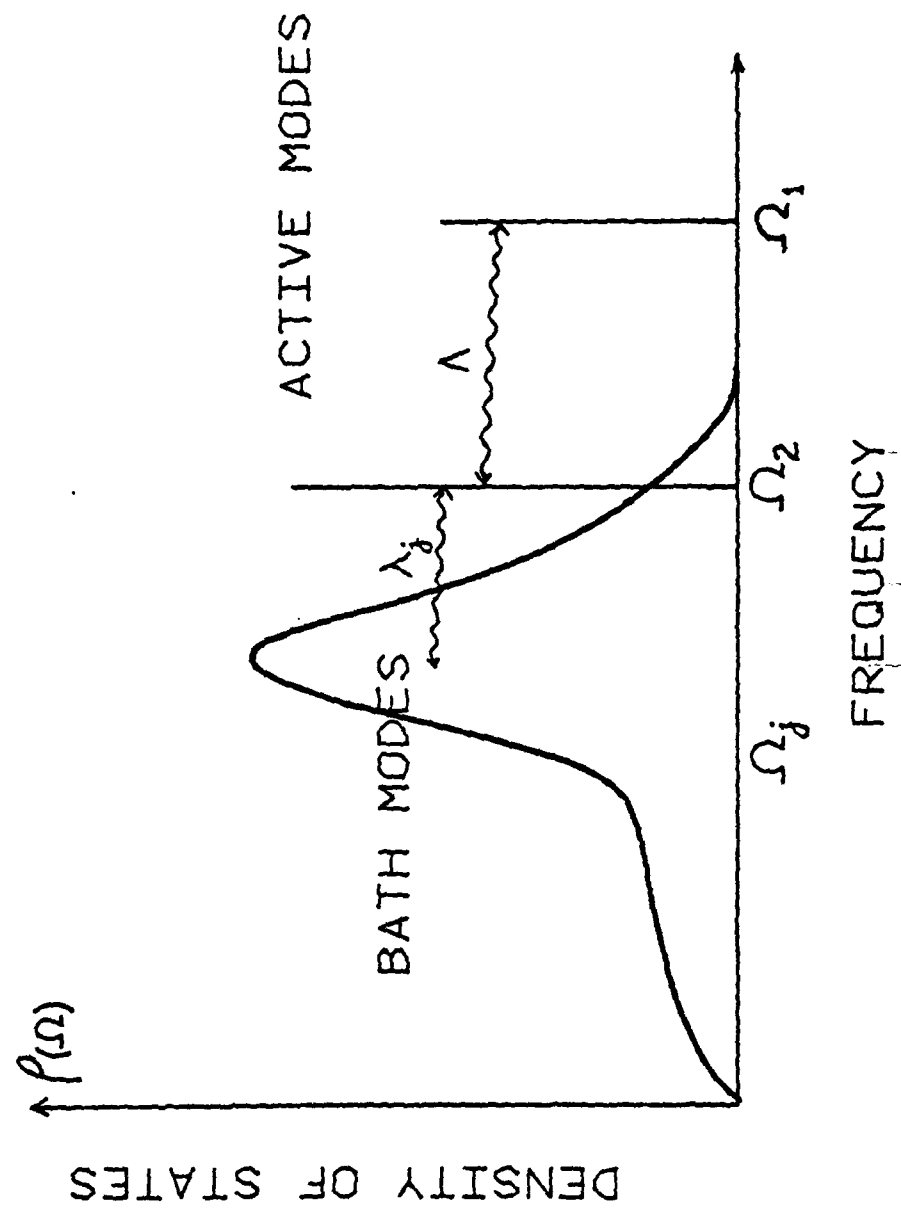


Fig. 2.

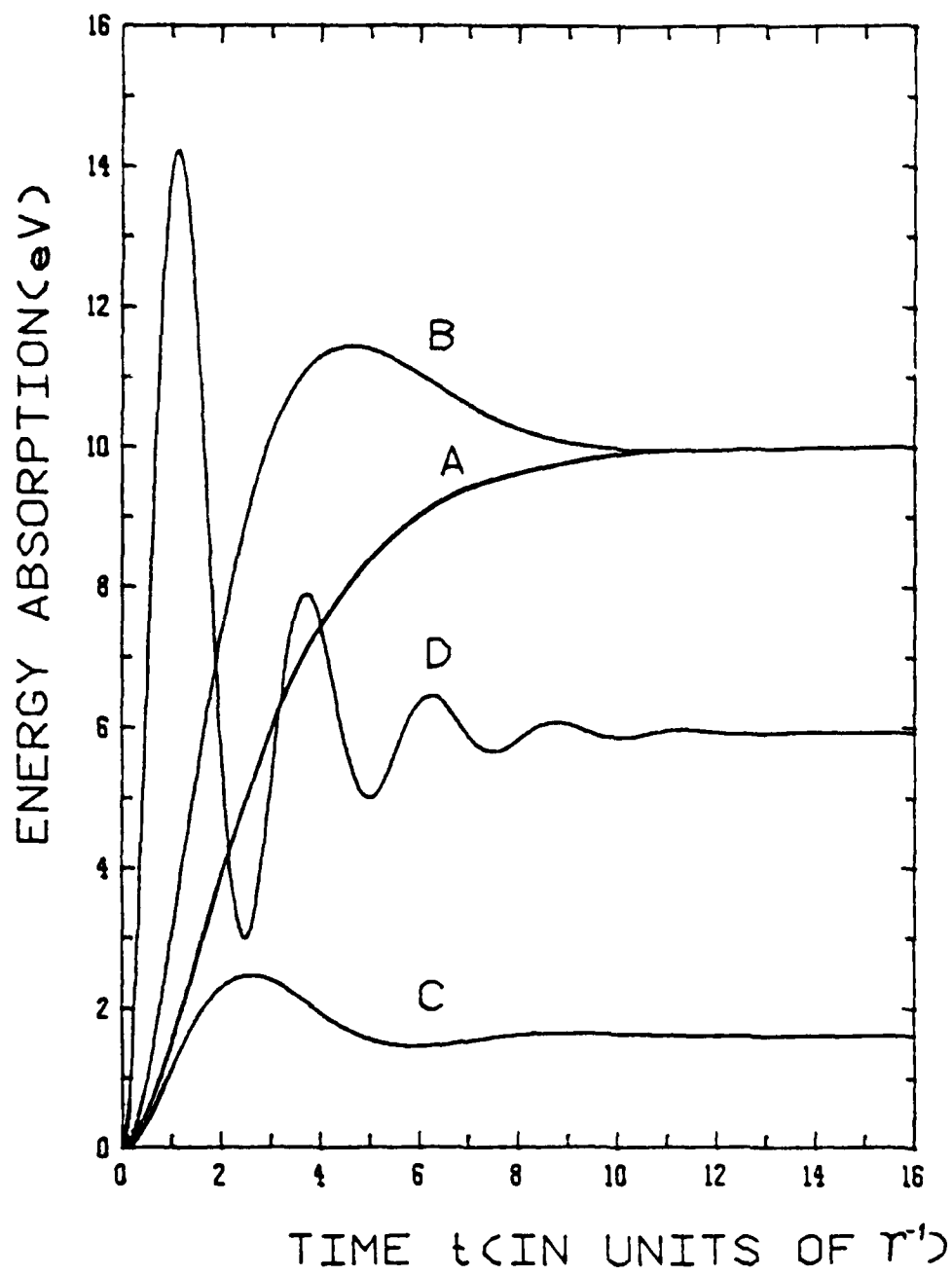


Fig. 3(A)

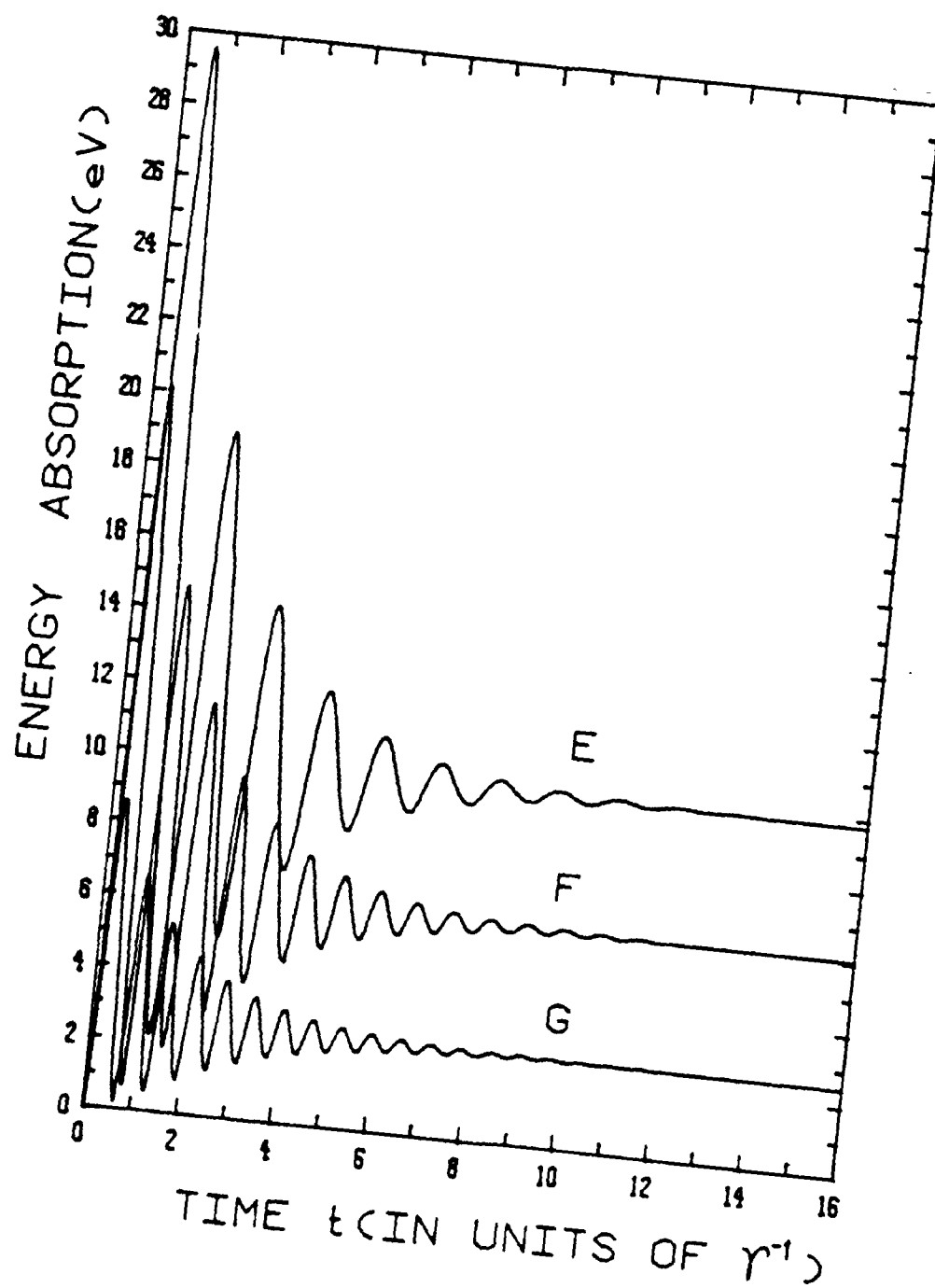


Fig. 3(B)

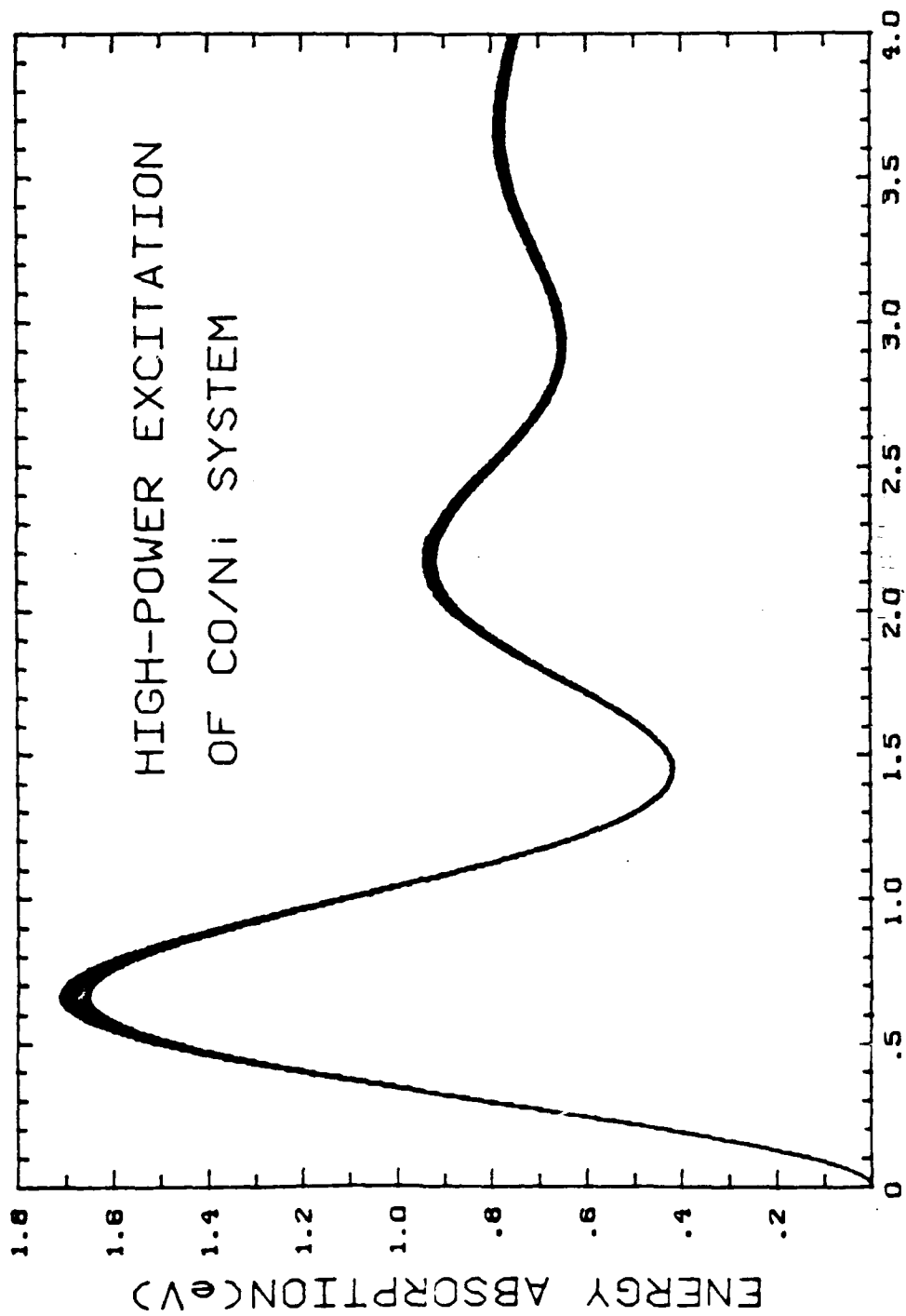


Fig. 4.

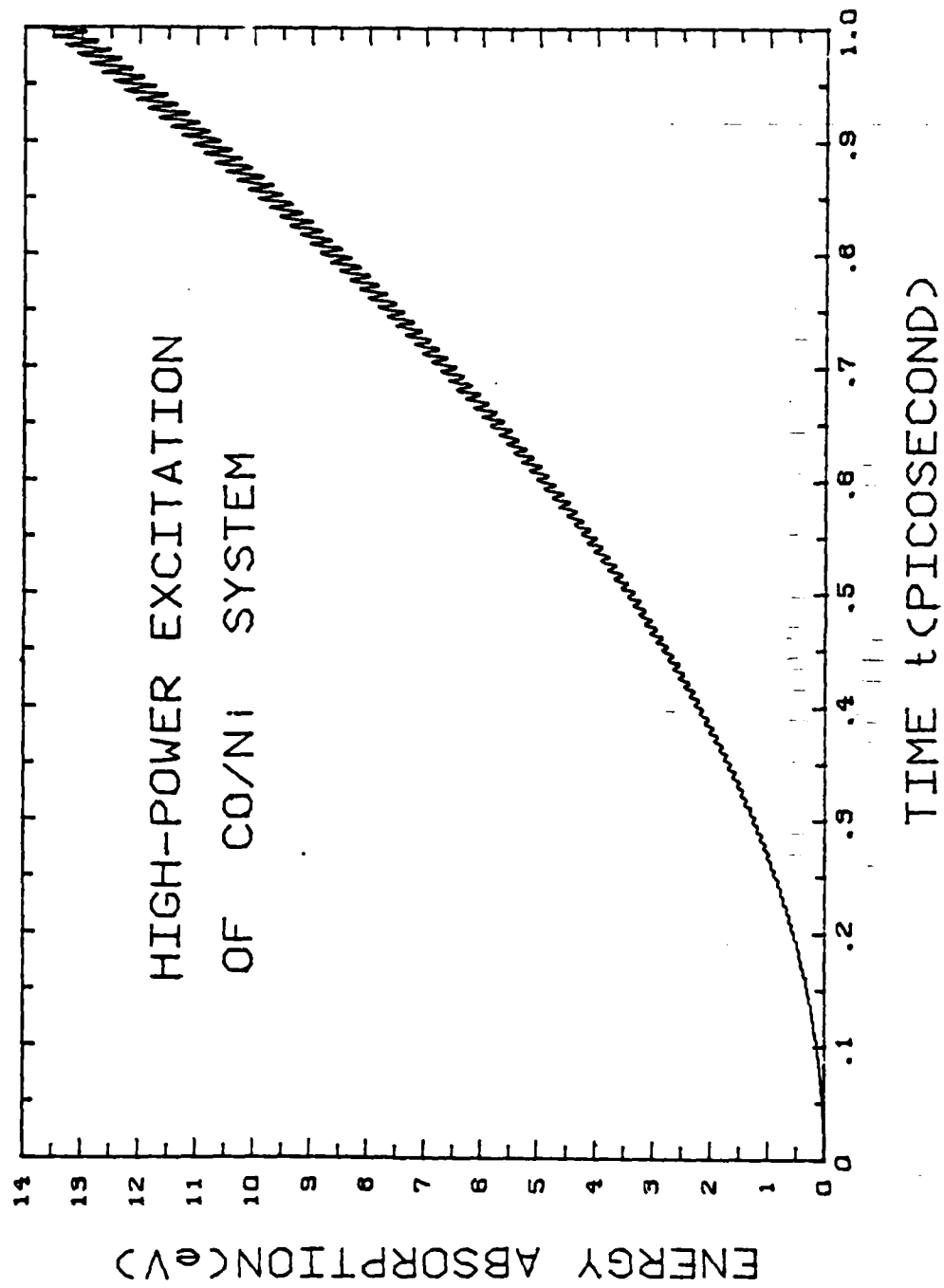


Fig. 5

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